Interface reconstruction in V-oxide heterostructures determined by x-ray absorption spectroscopy

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Abstract

We present an x-ray absorption study of the dependence of the V oxidation state on the thickness of LaVO$_3$ (LVO) and capping LaAlO$_3$ (LAO) layers in the multilayer structure of LVO sandwiched between LAO. We found that the change of the valence of V as a function of LAO layer thickness can be qualitatively explained by a transition between electronically reconstructed interfaces and a chemical reconstruction. The change as a function of LVO layer thickness is complicated by the presence of a considerable amount of V^{4+} in the bulk of the thicker LVO layers.

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The interfaces of hetero-junctions composed of transition-metal oxides have recently attracted great interest. For example, the interface between two band insulators $SrTiO_3$ (STO) and $LaAlO_3$ (LAO) is especially interesting due to its metallic [1] and even superconducting properties [2]. The interface between a band insulator STO and a Mott insulator $LaTiO_3$ (LTO) also exhibits metallic conductivity [3, 4, 5]. Recently Takizawa *et al.* [6] reported photoemission spectra of this interface with a clear Fermi cut-off, indicating a metallic interface layer. In this paper, we investigate the electronic structure of multilayers consisting of a band insulator LAO and a Mott insulator $LaVO_3$ (LVO). LAO is a band insulator with a large band gap of about 5.6 eV [7], whereas LVO is a Mott-Hubbard insulator with a Mott gap of about 1.0 eV [8]. One striking characteristic of this interface is the absence of a polar discontinuity because both LAO and LVO consist of alternating stacks of polar layers (LaO^+ and AlO_2^- or VO_2^-). Photoemission study of this interface has been reported in Refs. [9, 10, 11]. From the V $2p$ core-level spectra measured by soft x-ray [9] and hard x-ray [10, 11], the valence of V in LVO was found to be partially converted from V^{3+} to V^{4+} at the interface. Such a hole doping of LVO at the interface is expected to cause metallicity in this interface, but from the valence-band spectra [10], a Mott-Hubbard gap of LVO was found to remain open at the interface, indicating an insulating nature of this interface. This is consistent with transport studies showing increasing hole doping and conductivity with decreasing LAO thickness, but with an insulating temperature dependence [12]. The absence of metallicity is in contrast to the case of LAO/STO and LTO/STO, where electron doping of STO causes metallic conductivity at orders of magnitude lower carrier density than in LVO.

In this study we investigated the electronic structure of V oxide thin films by x-ray absorption spectroscopy (XAS). Regarding the determination of the valence of V, XAS has several advantages over photoemission spectroscopy (PES). XAS is rather bulk-sensitive with the average probing depth of > 50 Å in total-electron-yield (TEY) mode and > 200 Å in fluorescence-yield (FY) mode, whereas that of PES is at most ~ 50 Å even in the hard x-ray region. In the V $2p \rightarrow 3d$ XAS, a core hole is screened by an additional $3d$ electron, so XAS is more sensitive to the multiplet structure, and thus to the valence of V, than PES. XAS can be also applied to insulating materials due to its charge-neutral process. On the other hand, PES has a large advantage of detecting the valence-change-induced chemical shift and observing the structure near the Fermi level thus determining whether the system

is metallic or insulating.

From the XAS studies of LAO-sandwiched LVO thin films, we found that the V $2p$ XAS spectra depend on both the thickness of LVO and the thickness of the LAO capping layers. The dependence on LAO thickness can be qualitatively explained by the transition from an "electronic reconstruction" at the LAO/LVO interface to a "chemical reconstruction" involving surface off-stoichiometry [13], but that on LVO thickness indicates a more complex evolution.

The V oxide thin films were fabricated using the pulsed laser deposition (PLD) technique. The details of the sample fabrication and characterization are described in Refs. [9, 12, 14]. The characterization of the electronic structure of uncapped LVO thin films by x-ray photoemission spectroscopy is described in Ref. [15]. The films were grown on the TiO_2-terminated STO or AlO_2-terminated LAO substrates at an oxygen pressure of 10^{-6} Torr, except for $LaVO_4$ (10^{-2} Torr), using a KrF excimer laser ($\lambda = 248$ nm). Schematic views of the present thin films are shown in Fig. 1. Sample (a) was 50 uc $LaVO_4$ on STO without any capping layers as a reference for V^{5+}. Sample (b) was 50 uc $SrVO_3$ on STO without any capping layers as a reference for V^{4+}. Sample (c) consisted of y uc LVO sandwiched by x uc LAO and the LAO substrate. X-ray absorption experiments were performed at 11ID-1 (SGM) of the Canadian Light Source. The spectra were measured both in TEY and FY modes. As for the spectra we show in this paper, there was almost no difference between these two modes, so we show only the spectra measured in the TEY mode. Changing the exit slit width, which changes the experimental resolution from 90 to 800 meV, did not have an appreciable effect on the lineshape. Therefore, the total energy resolution was set to 800 meV in order to maximize intensities without sacrificing spectral details. All the spectra were measured at room temperature.

Figure 2 (a) shows the V $2p$ XAS spectrum of 50 uc $LaVO_4$ thin films on STO(001). The spectrum displayed sharp features characteristic of V^{5+} (d^0) oxides [16]. Figure 2 (b) shows the V $2p$ XAS spectrum of 50 uc $SrVO_3$ thin films on STO(001) with features characteristic of V^{4+}. Figure 2 (d) displays the mixed valent (V^{3+} and V^{4+}) character in the V $2p$ XAS spectra of LAO-sandwiched LVO thin films, where linear backgrounds have been subtracted as shown in Fig. 2 (c). The V $2p$ XAS spectra depend on the thickness of both LVO and LAO capping layers. By comparing these spectra with that of YVO_3 [17], the most sensitive region displaying V^{4+} character occurs around 520 eV, marked by an arrow in Fig. 2 (d).

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From this we note that even the (8, 3) sample contains a small amount of V^{4+}. To obtain a V^{3+} characteristic spectrum, the V^{4+} component (the spectrum of SVO (50 uc)/STO), which amounts to 5 % in this case, was subtracted from the spectrum of (8, 3).

By using this V^{3+} spectrum and the V $2p$ XAS spectrum of SVO (50 uc)/STO as V^{3+} and V^{4+} references, respectively, we can determine the average valence of V in the other samples. Figure 3 shows this determination of the valence of V by using a linear combination of V^{3+} and V^{4+}. The valence of V in (8, 3) is 3.05 as discussed above, and those of (3, 3), (8, 20), and (3, 20) were determined to be 3.45, 3.2, and 3.3 (±0.1), respectively.

In order to understand these results, we studied the following models. In the present samples, both the LAO and LVO layers are polar, and consist of alternating stacks of LaO^+ and AlO_2^- or VO_2^- layers. As recently discussed by Nakagawa *et al.* [18], electronic reconstruction [19] occurs at the interface of polar layers and nonpolar layers in order to prevent the divergence of Madelung potential, i.e., the so-called polar catastrophe [20]. When the V valence changes in the topmost LVO layer, the divergence of the electrostatic potential disappears in the LVO layers, but a dipole shift occurs in the LAO layers. This type of reconstruction is called "electronic reconstruction" as shown in Fig. 4 (b). This model assumes that the electronic reconstruction causes mixed valence of V only at one interface. In another case when surface off-stoichiometry (for example, O vacancies) occurs in the topmost LAO layer and part of the excess electrons created at the same time are transferred to the opposite side of the polar layer, the divergence of the electrostatic potential disappears as shown in Fig. 4 (c) [21]. In both cases, we can obtain the valence of V expected to be observed in XAS measurements. XAS measures a weighted average of V valence over the whole sample. The weighting is determined by the exponential decay of the secondary electron yield ($\propto \exp(-z/\lambda_e)$ from layers at a distance z from the outer surface). We present the results of this model calculation using the probing depths λ_e of 50, 200, and ∞ Å in Fig. 4 (a), showing only a weak dependence on the choice of λ_e. In experiment, the valence of V decreases with increasing LAO thickness, which is qualitatively consistent with the transition from electronically reconstructed interfaces to a chemical reconstruction to avoid the potential divergence in LAO layers. However, the change of the valence of V as a function of LVO layers is not systematic. The observed average valence is 3.2+ or 3.3+ in the (8, 20) and (3, 20) samples, respectively. The existence of such a large amount of V^{4+} cannot be explained by changing the valence of V from 3+ to 4+ only at the interface

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and suggests off-stoichiometry effects in the bulk of thick LVO layers. Such a change of the valence of V can be caused by excess O or deficiencies of La or V, and also influences the effects of the polar catastrophe in LVO layers.

In this study, we succeeded in determining the valence of V in multilayers composed of a band insulator LAO and a Mott insulator LVO by means of x-ray absorption spectroscopy. Here we made use of its sensitivity to bulk states and to the multiplet structure. We found that the V $2p$ XAS spectra depend on the thickness of both LVO and LAO capping layers. The dependence on LAO thickness can be explained by the transition from "electronic reconstruction" to "chemical reconstruction" involving surface off-stoichiometry with increasing thickness of LAO capping layers, but that on LVO thickness seems complicated by the presence of a considerable amount of V^{4+} in the thicker layers.

[1] A. Ohtomo and H. Y. Hwang, Nature **427**, 423 (2004).

[2] N. Reyren, S. Thiel, A. D. Caviglia, L. F. Kourkoutis, G. Hammer, C. Richter, C. W. Schneider, T. Kopp, A.-S. Ruetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, and J. Mannhart, Science **417**, 1196 (2007).

[3] A. Ohtomo, D. A. Muller, J. L. Grazul, and H. Y. Hwang, Nature **419**, 378 (2002).

[4] K. Shibuya, T. Ohnishi, M. Kawasaki, H. Koinuma, and M. Lippmaa, Jpn. J. Appl. Phys. **43**, L1178 (2004).

[5] S. Okamoto and A. J. Millis, Nature **428**, 630 (2004).

[6] M. Takizawa, H. Wadati, K. Tanaka, M. Hashimoto, T. Yoshida, A. Fujimori, A. Chikamtsu, H. Kumigashira, M. Oshima, K. Shibuya, T. Mihara, T. Ohnishi, M. Lippmaa, M. Kawasaki, H. Koinuma, S. Okamoto, and A. J. Millis, Phys. Rev. Lett. **97**, 057601 (2006).

[7] S.-G. Lim, S. Kriventsov, T. N. Jackson, J. H. Haeni, D. G. Schlom, A. M. Balbashov, R. Uecker, P. Reiche, J. L. Freeouf, and G. Lucovsky, J. Appl. Phys. **91**, 4500 (2002).

[8] T. Arima, Y. Tokura, and J. B. Torrance, Phys. Rev. B **48**, 17006 (1993).

[9] Y. Hotta, H. Wadati, A. Fujimori, T. Susaki, and H. Y. Hwang, Appl. Phys. Lett. **89**, 251916 (2006).

[10] H. Wadati, Y. Hotta, A. Fujimori, T. Susaki, H. Y. Hwang, Y. Takata, K. Horiba, M. Matsunami, S. Shin, M. Yabashi, K. Tamasaku, Y. Nishino, and T. Ishikawa, Phys. Rev. B **77**, 045122 (2008).

[11] M. Takizawa, Y. Hotta, T. Susaki, Y. Ishida, H. Wadati, Y. Takata, K. Horiba, M. Matsunami, S. Shin, M. Yabashi, K. Tamasaku, Y. Nishino, T. Ishikawa, A. Fujimori, and H. Y. Hwang, Phys. Rev. Lett. **102**, 236401 (2009).

[12] T. Higuchi, Y. Hotta, T. Susaki, A. Fujimori, and H. Y. Hwang, Phys. Rev. B **79**, 075415 (2009).

[13] Here we should note that there are three types of reconstruction. Electronic reconstruction involves a rearrangement of electrons keeping the total number of electrons the same. Ionic reconstruction involves a rearrangement of ions at the surface or interfaces forming a new structure which does not have a polarity discontinuity. Chemical reconstruction involves a change in the density of ions at the surface or interfaces.

[14] Y. Hotta, Y. Mukunoki, T. Susaki, H. Y. Hwang, L. Fitting, and D. A. Muller, Appl. Phys. Lett. **89**, 031918 (2006).

[15] H. Wadati, Y. Hotta, M. Takizawa, A. Fujimori, T. Susaki, and H. Y. Hwang, J. Appl. Phys. **102**, 053707 (2007).

[16] R. Zimmermann, R. Claessen, F. Reinert, P. Steiner, and S. Hufner, J. Phys.: Condens. Matter. **10**, (1998).

[17] H. F. Pen, M. Abbate, A. Fuijmori, Y. Tokura, H. Eisaki, S. Uchida, and G. A. Sawatzky, Phys. Rev. B **59**, 7422 (1999).

[18] N. Nakagawa, H. Y. Hwang, and D. A. Muller, Nature Materials **5**, 204 (2006).

[19] R. Hesper, L. H. Tjeng, A. Heeres, and G. A. Sawatzky, Phys. Rev. B **62**, 16046 (2000).

[20] W. A. Harrison, E. A. Kraut, J. R. Waldrop, and R. W. Grant, Phys. Rev. B **18**, 4402 (1978).

[21] Here we have to consider only the top surface because the compensating charge on the other side has to be there for charge neutrality but does not further affect our spectroscopy.

Figure captions

Fig. 1. (Color online) Schematic view of the samples. (a) $LaVO_4$ (50 uc)/$SrTiO_3$. (b) $SrVO_3$ (50 uc)/$SrTiO_3$. (c) $LaAlO_3$ (x uc)/$LaVO_3$ (y uc)/$LaAlO_3$.

Fig. 2. (Color online) V $2p$ XAS spectra. (a) $LaVO_4$ (50 uc)/$SrTiO_3$. (b) $SrVO_3$ (50 uc)/$SrTiO_3$. (c) $LaAlO_3$ (x uc)/$LaVO_3$ (y uc)/$LaAlO_3$ in a wide energy region. (d) $LaAlO_3$ (x uc)/$LaVO_3$ (y uc)/$LaAlO_3$ after subtracting backgrounds.

Fig. 3. (Color online) Determination of the valence of V by using a linear combination of V^{3+} and V^{4+}. (a) (8, 3), (b) (3, 3), (c) (8, 20), (d) (3, 20).

Fig. 4. (Color online) Comparison of the valence of V between experiment and the reconstruction model. Panel (a) shows the comparison between experiment and the model, and panels (b) and (c) show the electronic and chemical reconstruction, respectively.

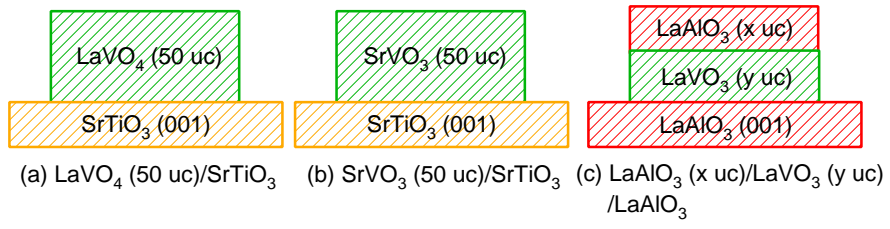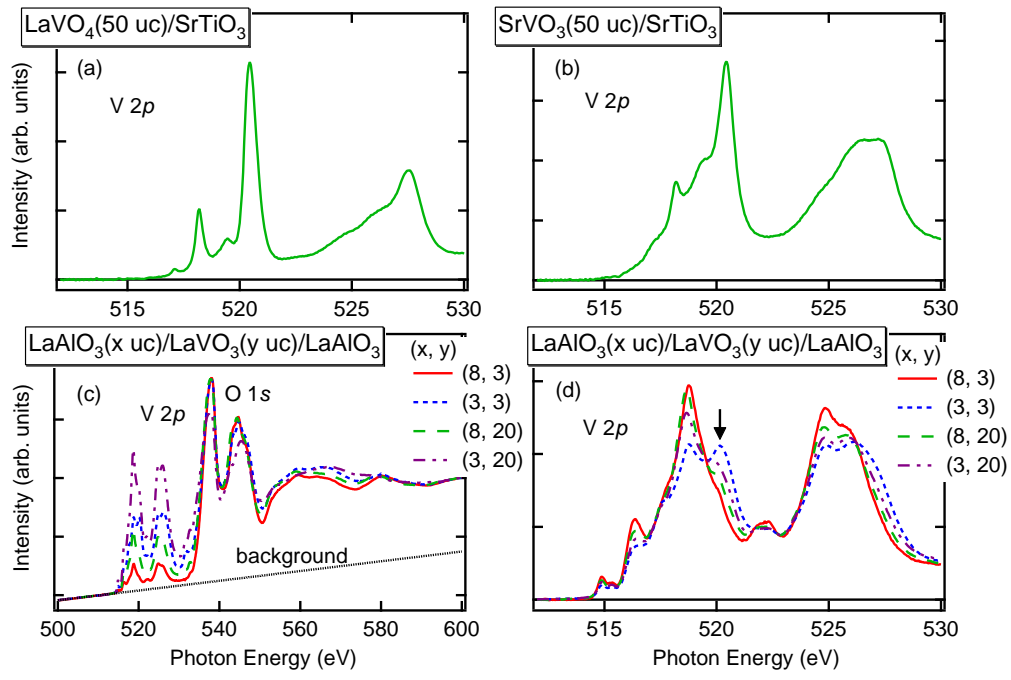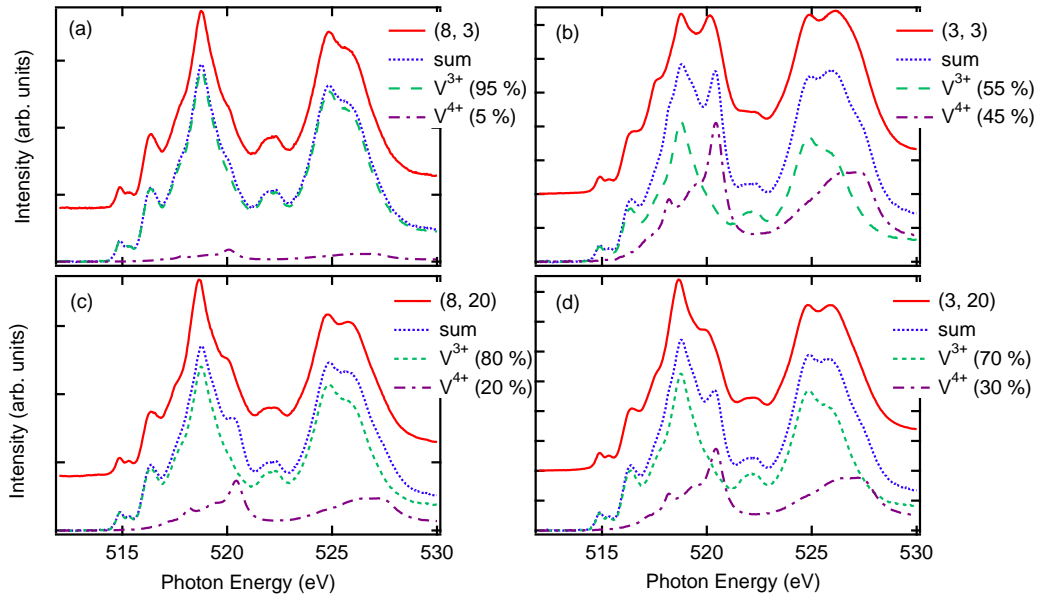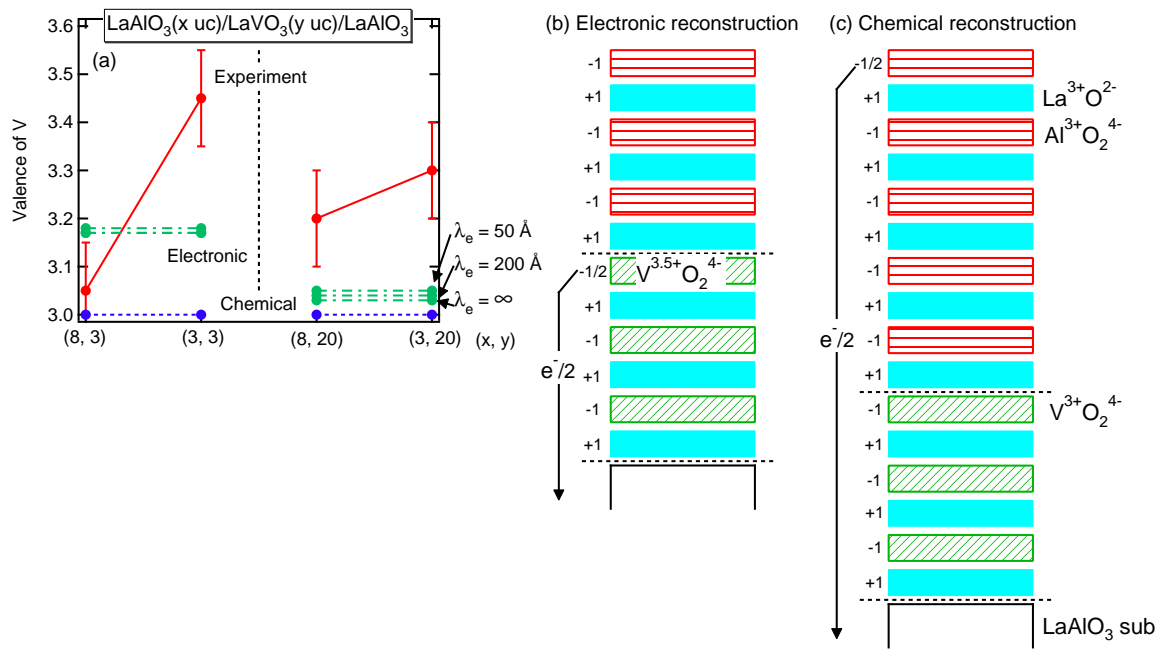(a) LaVO$_4$ (50 uc)/SrTiO$_3$ (b) SrVO$_3$ (50 uc)/SrTiO$_3$ (c) LaAlO$_3$ (x uc)/LaVO$_3$ (y uc) /LaAlO$_3$

FIG. 1:

FIG. 2:

FIG. 3:

FIG. 4: